Specialty Gas Instrumentation

By Ray Borzio, Mike Lee, and Scott Varian

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Gases and welding distributors continue to have a significant future in the production, delivery, and related services for specialty gases. In the July 2009 issue of *CryoGas International* we introduced our expanded focus on specialty gases with three feature articles. This month we continue to examine the importance of instrumentation and analytical equipment in the supply chain for the production and use of specialty gases, a fast growing market.

Analytical equipment and instruments play an important role in the production operations of specialty gases. Having knowledge and understanding of this instrumentation and its many uses in laboratories and operations is important. This article looks at analytical equipment from the viewpoint of a distributor's specialty gases production and also from the perspective of the instrumentation needs of a distributor's customers.

SELECTING A GAS ANALYZER

The selection of the appropriate gas analyzer and related equipment is an important activity as it relates to the growth of a gas distributor's specialty gas business. Here we look at selecting a gas analyzer using the example of a distributor who fills industrial and medical gases and receives cryogenic argon, cryogenic nitrogen, and gaseous helium in bulk (tube trailers).

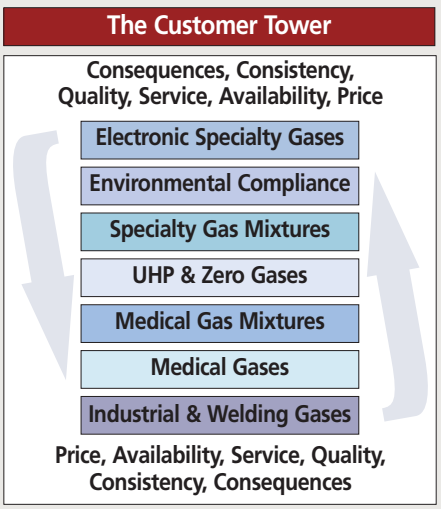

Figure 1 Source: Special Gas Services

Technology plays a large role in the specialty gas business, and as specialty gases applications move up the customer tower (see Figure 1) of market segments, technology, and capital investment costs increase. *(We described the concept of a customer tower in "Gases That Carry a Guarantee" CGI, July 2009, p. 32.)* The tower plays into all aspects of the growth of your gas business, setting up entry and development points to that business. When moving up the tower, that is, selling specialty gases into a technical/product block higher than your current capability, a distributor can buy gases from a major gas company with adequate capabilities rather than investing in new production capability. A common mistake made by distributors that want to service a new technical/product block is to purchase an analyzer and related equipment to service those blocks, then discovering that this investment has limited application beyond that new product. The instruments purchased for one product may not have the sensitivity, precision, or appropriate options to serve broader spec gas needs or those in the next higher block.

To make reasoned investments in analytical equipment in order to grow or develop your specialty gas business, consider this list of questions when making purchasing decisions along the supply chain.

Are bulk nitrogen, argon, and helium delivered as UHP (Ultra High Purity) together with a COA (certificate of analysis) from your supplier? The COA must include at a minimum, trace oxygen, trace water, total hydrocarbons, and trace nitrogen contaminant levels.

If the answer is YES, you need to confirm that that these gases are true UHP and this requires the purchase a good trace oxygen analyzer (about $5,000). An analyzer will serve as the work-horse and QA (quality assurance) heart of your UHP gas filling process. Once you determine that the gases delivered to you are UHP grade, you must confirm when you re-package these gases for distribution, that they have not been contaminated in the process. To do this, fill a batch of nitrogen cylinders and analyze each one for oxygen content. If you are fortunate, the oxygen content in the filled batch will be unchanged from the content reported in the bulk gas COA when delivered.

As specialty gas grades routinely demand readings at < 1 ppm, the best choice for trace oxygen analysis is an electrolytic cell equipped with an option that will allow for trace oxygen analysis in carbon dioxide to qualify as Anaerobic (low oxygen) Grade. This option can not be easily added later. We advise against the purchase of a trace oxygen analyzer with a zirconia sensor as trace hydrocarbons present may interfere with the sensor's response to oxygen and give a fictitiously low reading. Zirconia sensor-based detectors are typically only recommended down to the 20 ppm range.

If the answer to the above question in NO, you must demand UHP with a COA or get another supplier if you want to distribute specialty gases.

Has the oxygen level in your filled cylinder batch changed significantly from the level of the incoming bulk liquid oxygen (LOX)?

If the answer is YES, check your system for obvious leaks. Review your fill procedures. Purchase a vacuum meter capable of reading in microns of mercury (about $600). Determine if your vacuum systems are capable of attaining and holding a vacuum of 100 microns or better. This vacuum level must hold when the vacuum pump is isolated from the manifold and the vacuum meter probe is monitoring the manifold. If oxygen readings are not consistent, consider converting the

cylinder valve population to the diaphragm packless type, or, at a minimum, replace the valve packings as in-board leaks commonly occur through worn packings. Make necessary changes to equipment and packages.

If the answer to the above question in NO, purchase a good trace moisture analyzer (about $8,500), then fill a batch of cylinders with nitrogen to the best of your ability. Analyze every cylinder in the batch for moisture content. Be sure to specify an analyzer cell that is suitable for oxygen service as well as for inert gases as you will also want to check Aviator's Breathing Oxygen for moisture.

Do all of your cylinders meet moisture specifications?

If the answer is YES, purchase a total hydrocarbon analyzer (about $11,000) and check the batch for total hydrocarbons expressed as methane. Be sure to invest in a unit with a catalytic methanizer capability that allows for the detection of carbon monoxide and carbon dioxide combined, as this is a typical specification for higher grades of zero air. It is best to add a hydrocarbon analyzer at this point as it is not easily added later on.

If the answer to the above question is NO, purchase a cylinder bake-out system (about $25,000) as the water is likely off-gassing from the cylinder walls. *(For more on bake-out systems see "What's So Special about Specialty Gases?", CGI, July 2009, p. 44.)*

Nitrogen content is not always reported since N_2 is not a containment of interest in most applications. Do your company's product specifications require you to report trace nitrogen in your helium and argon?

If the answer is YES, note the change in oxygen content between the incoming bulk supply and the fill batch. Multiply this difference by four and add it to the incoming bulk trace nitrogen content. This will estimate the nitrogen content in the fill batch.

If the answer to the above question is NO, we recommend that your company specify trace nitrogen if you are serious about moving up the specialty gas customer tower.

BUSINESS BEYOND THE ANALYZER

To operate at the UHP and Zero Grade level on the customer tower, a distributor has invested about $25,000 on analytical instruments including analyzers for trace oxygen, trace moisture, and total hydrocarbons — what we refer to as "the eyes to see." In many cases, this investment exposes deficiencies in the filling operations that will result in additional plant equipment and capital expense. At the UHP and Zero Grade level, the ability to analyze for trace nitrogen is not that crucial. To proceed to the next level on the tower, however, you must consider the importance of actually *analyzing* for the trace nitrogen contamination, which we only estimated thus

Caption

far. At higher levels on the customer tower the number for nitrogen impurity needs to be quantified and doing this requires large investments in additional equipment. There are three approaches a distributor may take to get to the next level.

The first is a low-tech approach that requires the distributor to buy additional process analyzers that will be specific for only trace nitrogen in helium or argon. These analyzers are very limited, typically designed to measure the spectral emission of argon. They only detect trace nitrogen, with a separate analyzer required for both argon and helium. These process-type analyzers cost about $14,000 each, so the complete trace contaminant price tag would exceed $50,000, including all the bells and whistles (see estimates above).

The second approach is to invest in a gas chromatograph (GC) that performs all of the above on a single instrument using a discharge ionization detector (DID). These can cost about $45,000, which sounds like a bargain, but never is, in our opinion. Purchasing this instrument prematurely is a common mistake among distributors contemplating expanding their specialty gas business. A gas distributor contemplating pure gas production may not understand that a degreed chemist is required to analyze UHP helium for assay using a gas chromatograph. This is a costly employee. We suggest distributors stick with process instruments that are designed to be easily calibrated with a certified standard, and then produce a real impurity number on a digital display. The GC DID detector has justifiable application only at very high purity levels, such as those used in the semiconductor industry, where very few distributors do business.

Chromatography, however, does become useful to distributors that wish to move up the tower to the specialty gas mixtures block, depending on the type of mixtures they intend to produce. A distributor that intends to produce only two component mixtures will need to purchase a binary gas analyzer (about $4,500) but not a GC. These analyzers employ our industry's most reliable detection methods — thermal conductivity. They measure a gas' ability to conduct heat away from a hot wire, because no two gases do this at the same rate. These analyzers are limited to binary gas mixtures but are suitable for virtually any combination of two gases at concentrations of about one percent or higher.

A distributor that plans to produce multiple component mixtures, however, should invest in a basic gas chromatograph (about $15,000). This gas chromatograph will have the same type of detector as the binary gas analyzer but will have the ability to analyze multiple component mixtures.

Your investment in mixture analysis will be approximately $20,000 with the binary gas analyzer and a basic gas chromatograph. You can improve on this capability, and save some money, using a third approach — micro-GC technology. This technology allows you to perform your basic mixture analysis as well as capture the trace nitrogen impurity number in your argon and helium. It also eliminates the need for the binary gas analyzer, the basic GC, and the need for the two process analyzers that give you the trace nitrogen number in helium and argon (described above). This type of gas chromatograph packages the thermal conductivity detector, columns, injectors, and valving using very advanced micro machining techniques and silicon technology resulting in a very efficient modular analysis system. The result is very high sensitivity coupled with speed of analysis and a software-based, user-

friendly PC operating system. With micro-GC technology you have a complete specialty gas lab, capable of analyzing multiple component mixtures, for an approximate investment of $65,000. Add another $10,000 for specialty gas regulator stations and your lab is complete.

KEEPING GASES PURE ALONG THE SUPPLY CHAIN

Distributors who transfill or repackage high-purity gases take great measures to be sure the processes are not compromised by impurities such as oxygen, moisture, and particulates. The processes include pulling vacuums, purges, cylinder bake outs, and much more. To do this without introducing impurities, there is a variety of high-purity and analytical equipment required.

All of the connecting equipment must be suited for high-purity service and the specifications designed to accommodate the specified minimums of impurities including: pieces from bulk storage; parts that connect into the lab and the analytical equipment; and, the connecting equipment into the cylinder for checking and delivery to the customer. For example, regulators used in the transfill or repackaging process should be of brass or stainless steel construction with metal diaphragms. Regulators with forged bodies and/or neoprene or rubber diaphragms are not suitable for these processes as they can trap impurities and allow them into the high-purity system. Piping and valves must be carefully considered as well. Valves should be of the diaphragm, packless type as ball and needle valves may allow impurities into the system.

Other important aspects of this process are the vacuum and/or purge cycles. By performing these efficiently, any contamination that has entered the process during initial start up, or cylinder change outs, will be eliminated.

Specialty gas distributors should also provide best practices information on using the correct equipment to ensure gas flowing from their delivered cylinder to the instrument or process in the customer's operations or lab. Following procedures the first time is critical as the first complaint for instrument failure is most often "the gas is bad." Distributors who follow the correct procedures and use the proper equipment during these operations can be assured of delivering quality specialty gases to their customers.

BRINGING SPECIALTY GASES TO MARKET

When investigating specialty gas market opportunities we strongly advise distributors to seek the expertise of a firm that has broad industry knowledge at various levels of specialty gases. Industry experts can walk you through the appropriate steps in choosing the correct equipment for your internal lab. The analytical equipment and procedures discussed above are paramount to the success of a distributor's effort to bring specialty gases to the marketplace. If any one step is eliminated, failure is at hand. And in specialty gas markets, like the Life Sciences, failure to deliver top quality gases can quickly become a much larger problem. With very high customer expectations, the news of "bad gas" spreads like wildfire.

A specialty gas salesperson does not have to become a chemist to be successful, but direct knowledge of the steps a cylinder must go through to get into the "Specialty Gas" family is very important. Your salesperson must be able to "talk the talk" and "walk the walk" with the customer. Customers use specialty gases to feed analytical equipment that is even more expensive than the instruments the distributor needs to assure quality, so understanding customer requirements is essential.

High-speed mass spectrometers (MS) and high-efficiency gas chromatographs are just two of the instruments that utilize these gases. A MS or GC that is fed a contaminated gas will automatically shut down its process. Shutting down a string of fifteen MS machines, costing $500,000 each, with a gas that should never have left your process lab, can halt $7.5 million worth of analytical equipment. This type of catastrophe will be the responsibility of the customer's lab manager or facility manager, and their first phone call to remedy the situation will be to their gas supplier.

To avoid that call from the lab manager, make certain all of the procedures discussed in this article are in place before any gases leave your plant. Cutting corners in the specialty gas lab does not pay off — ever. Make sure you establish and keep a reputation for delivering a very high-quality product with consistent performance. Get good direction from, and seek the guidance of, the very best in the industry. The equipment described above is a rock solid requirement to the production of specialty gases, as is its efficient use. Produce your gases correctly using the proper instrumentation and equipment, educate your sales staff to the extreme, and enjoy the longevity of specialty gases' higher margins in a rapid growth market.

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